

Excited states of spherium

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We report analytic solutions of a recently discovered quasi-exactly solvable model consisting of two electrons, interacting *via* a Coulomb potential, but restricted to remain on the surface of a \mathcal{D} -dimensional sphere. Polynomial solutions are found for the ground state, and for some higher ($L \leq 3$) states. Kato cusp conditions and interdimensional degeneracies are discussed.

Keywords: Exact solution, excited states, spherium, cusp condition, interdimensional degeneracies

I. INTRODUCTION

A quasi-exactly solvable model is one for which it is possible to solve the Schrödinger equation exactly for a finite portion of the energy spectrum [1]. In quantum chemistry, a famous example of this is the Hooke's law atom [2–5], which consists of a pair of electrons, repelling Coulombically but trapped in a harmonic external potential. This model and others [6–12] have been used extensively to test various approximations [13–20] within density functional theory (DFT) [21–23] and explicitly correlated methods [24–28].

We have recently discovered [29] that a pair electrons, repelling Coulombically but constrained to remain on the surface of a \mathcal{D} -sphere of radius R [17, 30–37] is also quasi-exactly solvable and we have called this system \mathcal{D} -spherium. (We adopt the convention that a \mathcal{D} -sphere is the surface of a $(\mathcal{D}+1)$ -dimensional ball.) We have shown that the Schrödinger equation for the 1S and the 3P states of \mathcal{D} -spherium can be solved exactly for a countably infinite set of R values and that the resulting wave functions are polynomials in the interelectronic distance $0 \leq u \equiv |\mathbf{r}_1 - \mathbf{r}_2| \leq 2R$.

In this article, we extend our earlier results [29] to higher angular momentum (up to $L = 3$) states of \mathcal{D} -spherium ($\mathcal{D} \geq 2$) for both the singlet and triplet manifolds. The $\mathcal{D} = 1$ case is anomalous and, for brevity, is not discussed here. We use atomic units throughout.

II. WAVE FUNCTION

The Hamiltonian of \mathcal{D} -spherium is

$$\hat{H} = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) + \frac{1}{u}, \quad (1)$$

where the two first terms represent the kinetic contribution of each electron, and u^{-1} is the Coulomb operator.

Following Breit [38], we write the total wave function as the product

$$\Phi(\{s_1, s_2\}, \{\boldsymbol{\Omega}_1, \boldsymbol{\Omega}_2\}, u) = \Xi(s_1, s_2) \chi(\boldsymbol{\Omega}_1, \boldsymbol{\Omega}_2) \Psi(u), \quad (2)$$

where Ξ , χ and Ψ are the spin, angular and interparticle wave functions, respectively, and s_i and $\boldsymbol{\Omega}_i$ are the spin and hyperspherical coordinates [39] of the i -th electron. The singlet and triplet wave functions are given by the familiar [40] forms

$$^1\Xi(s_1, s_2) = \frac{1}{\sqrt{2}} [\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)], \quad (3)$$

$$^3\Xi(s_1, s_2) = \begin{cases} \alpha(s_1)\alpha(s_2), \\ \frac{1}{\sqrt{2}} [\alpha(s_1)\beta(s_2) + \beta(s_1)\alpha(s_2)], \\ \beta(s_1)\beta(s_2). \end{cases} \quad (4)$$

The angular part is associated with an energy

$$E_\chi = \frac{\Lambda}{R^2}, \quad (5)$$

$$\Lambda = \frac{\ell_1(\ell_1 + \mathcal{D} - 1)}{2} + \frac{\ell_2(\ell_2 + \mathcal{D} - 1)}{2}, \quad (6)$$

where ℓ_1 and ℓ_2 are the angular momentum quantum numbers of the corresponding one-electron configuration ($s = 0$, $p = 1$, $d = 2$, $f = 3$, ...). The functions χ , which are dependent on the nature of the state considered [38, 41], are gathered in Table I, where $\theta_i \in [0, \pi]$ and $\phi_i \in [0, 2\pi]$ are the $(\mathcal{D} - 1)$ -th and \mathcal{D} -th hyperspherical angles of the electron i . The corresponding one-electron configurations are also reported. In Table I, the suffixes e (even) and o (odd) are related to the parity of the states, which is given by $(-1)^{\ell_1 + \ell_2}$. Hence, we label the states with the notation $^{1,3}L^{e,o}$, where $L = S, P, D, F, \dots$

III. POLYNOMIAL SOLUTIONS

Substituting the ansatz (2) into the Hamiltonian (1) yields the Schrödinger equation

$$\left(\frac{u^2}{4R^2} - 1 \right) \frac{d^2\Psi}{du^2} + \left(\frac{\delta u}{4R^2} - \frac{1}{\gamma u} \right) \frac{d\Psi}{du} + \frac{\Psi}{u} = E\Psi, \quad (7)$$

where the parameters δ and γ are tabulated for each state in Table I.

By introducing the dimensionless variable $x = u/2R$, Eq. (7) can be recast as a Heun's differential equation [42] with singular points at $x = -1, 0, +1$. Following

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TABLE I. Ground state and excited states of \mathcal{D} -spherium

State	Configuration	$\chi(\Omega_1, \Omega_2)$	δ	γ^{-1}	Λ	κ	Transformation
$^1S^e$	s^2	1	$2\mathcal{D} - 1$	$\mathcal{D} - 1$	0	0	$^3P^e$
$^3P^o$	sp	$\cos \theta_1 - \cos \theta_2$	$2\mathcal{D} + 1$	$\mathcal{D} + 1$	$\mathcal{D}/2$	1	$^1D^o$
$^1P^o$	sp	$\cos \theta_1 + \cos \theta_2$	$2\mathcal{D} + 1$	$\mathcal{D} - 1$	$\mathcal{D}/2$	0	$^3D^o$
$^3P^e$	p^2	$\sin \theta_1 \sin \theta_2 \sin(\phi_1 - \phi_2)$	$2\mathcal{D} + 3$	$\mathcal{D} + 1$	\mathcal{D}	1	
$^3D^e$	sd	$\chi_{^3P^o} \cdot \chi_{^1P^o}$	$2\mathcal{D} + 3$	$\mathcal{D} + 1$	$\mathcal{D} + 1$	1	$^1F^e$
$^1D^o$	pd	$\chi_{^3P^o} \cdot \chi_{^3P^e}$	$2\mathcal{D} + 5$	$\mathcal{D} + 3$	$3\mathcal{D}/2 + 1$	2	
$^3D^o$	pd	$\chi_{^1P^o} \cdot \chi_{^3P^e}$	$2\mathcal{D} + 5$	$\mathcal{D} + 1$	$3\mathcal{D}/2 + 1$	1	
$^1F^e$	pf	$\chi_{^3P^e} \cdot \chi_{^3D^e}$	$2\mathcal{D} + 7$	$\mathcal{D} + 3$	$2\mathcal{D} + 3$	2	

the known solutions of this equation [43], we seek wave functions of the form

$$\Psi(u) = \sum_{k=0}^{\infty} a_k u^k, \quad (8)$$

and substitution into (7) yields the three-step recurrence relation

$$a_{k+2} = \frac{\gamma}{(k+2)[(k+1)\gamma+1]} \left\{ a_{k+1} + \left[\frac{k(k+\delta-1)}{4R^2} - E \right] a_k \right\}, \quad (9)$$

with the starting values $a_0 = 1$ and $a_1 = \gamma$.

If the series (8) terminates at a certain $k = n$, we obtain the exact wave function

$$\Psi_{n,m}(u) = \sum_{k=0}^n a_k u^k, \quad (10)$$

for a particular radius $R_{n,m}$ and energy $E_{n,m}$. This is an n th degree polynomial with m nodes between 0 and $2R$ ($0 \leq m \leq \lfloor \frac{n+1}{2} \rfloor$) and requires that a_{n+1} and a_{n+2} vanish. If $a_{n+1} = 0$, the relation

$$R_{n,m}^2 E_{n,m} = \frac{n}{2} \left(\frac{n}{2} + \frac{\delta-1}{2} \right) \quad (11)$$

ensures that $a_{n+2} = 0$. For a given n , the energies are thus determined by finding the roots of the equation $a_{n+1} = 0$, which is a polynomial in E , of degree $\lfloor \frac{n+1}{2} \rfloor$.

For the $^1D^e$ state, we have not been able to obtain polynomial solutions because the Hamiltonian (1) is not separable using the ansatz (2) and the wave function satisfies exchange coupled equations [44]. This applies also to some other states of higher angular momentum.

IV. RESULTS AND DISCUSSION

Numerical values of the energies and radii for the $^1P^o$ and $^3P^e$ states are reported in Tables II and III. Tables containing results for the $^1S^e$ and $^3P^o$ states can be found

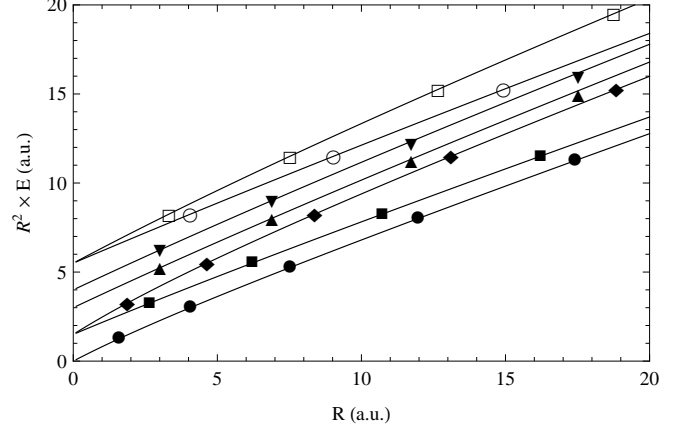


FIG. 1. Energy of the S , P and D states of 3-spherium. ($^1S^e < ^3P^o \leq ^1P^o < ^3P^e < ^3D^e < ^1D^o \leq ^3D^o$). The quasi-exact solutions are shown by the markers.

in Ref. [29]. Numerical values of the energies and radii for the higher angular momentum states can be determined using the interdimensional degeneracies (see Sec. IV E).

For any given state, as n increases, the radius increases and the energy decreases. The opposite behavior is observed with respect to m . Furthermore, as R (or, equivalently, n) increases, the electrons tend to localize on opposite sides of the sphere due to the dominance of the Coulomb interaction as the density decreases [34, 35]. Such Wigner crystallization [45] has also been observed in other systems [5, 10, 46].

The energies of the S , P and D states ($m = 0$) for 3-spherium are plotted in Fig. 1 (the quasi-exact solutions are indicated by markers), while density plots of 2-spherium ($n = 1$ and $m = 0$) are represented on Fig. 2.

A. Natural/unnatural parity

In attempting to explain Hund's rules [47] and the "alternating" rule [48, 49] (see also [50, 51]), Morgan and

TABLE II. Radii $R_{n,m}$ and energies $E_{n,m}$ for $^1P^\circ$ states of two electrons on a \mathcal{D} -sphere ($\mathcal{D}=2,3,4$)

	n/m	$\mathcal{D} = 2$				$\mathcal{D} = 3$				$\mathcal{D} = 4$			
		0	1	2	3	0	1	2	3	0	1	2	3
Radius	1	1.118				1.871				2.598			
	2	3.162				4.637				6.083			
	3	6.226	1.656			8.376	2.520			10.52	3.303		
	4	10.30	4.232			13.11	5.888			15.93	7.440		
	5	15.38	7.847	2.159		18.84	10.21	3.127		22.32	12.49	3.966	
	6	21.46	12.49	5.246		25.57	15.53	7.077		29.72	18.51	8.732	
	7	28.54	18.14	9.397	2.639	33.30	21.84	11.97	3.707	38.11	25.51	14.39	4.599
	8	36.63	24.80	14.59	6.222	42.03	29.15	17.86	8.220	47.49	33.49	21.01	9.976
Energy	1	1.000				0.5000				0.3333			
	2	0.3000				0.1860				0.1351			
	3	0.1355	1.914			0.09622	1.063			0.07460	0.7562		
	4	0.07541	0.4467			0.05820	0.2884			0.04731	0.2168		
	5	0.04757	0.1827	2.414		0.03874	0.1319	1.406		0.03260	0.1041	1.033	
	6	0.03257	0.09620	0.5450		0.02753	0.07468	0.3594		0.02378	0.06129	0.2754	
	7	0.02363	0.05851	0.2180	2.764	0.02051	0.04771	0.1587	1.656	0.01808	0.04035	0.1267	1.241
	8	0.01789	0.03903	0.1127	0.6200	0.01585	0.03295	0.08781	0.4144	0.01419	0.02853	0.07252	0.3215

TABLE III. Radii $R_{n,m}$ and energies $E_{n,m}$ for $^3P^\circ$ states of two electrons on a \mathcal{D} -sphere ($\mathcal{D}=2,3,4$)

	n/m	$\mathcal{D} = 2$				$\mathcal{D} = 3$				$\mathcal{D} = 4$			
		0	1	2	3	0	1	2	3	0	1	2	3
Radius	1	2.291				3.000				3.708			
	2	5.477				6.892				8.307			
	3	9.616	3.006			11.72	3.748			13.84	4.478		
	4	14.73	6.851			17.52	8.334			20.32	9.797		
	5	20.84	11.62	3.676		24.30	13.82	4.453		27.78	16.01	5.208	
	6	27.94	17.35	8.156		32.07	20.26	9.708		36.22	23.15	11.22	
	7	36.04	24.05	13.54	4.315	40.83	27.66	15.84	5.128	45.65	31.25	18.10	5.909
	8	45.13	31.75	19.86	9.412	50.58	36.04	22.90	11.03	56.07	40.32	25.89	12.60
Energy	1	0.3333				0.2500				0.2000			
	2	0.1333				0.1053				0.08696			
	3	0.07300	0.7472			0.06002	0.5874			0.05093	0.4862		
	4	0.04607	0.2131			0.03908	0.1728			0.03390	0.1459		
	5	0.03166	0.1019	1.018		0.02752	0.08503	0.8196		0.02429	0.07315	0.6913	
	6	0.02306	0.05983	0.2706		0.02042	0.05117	0.2228		0.01829	0.04477	0.1906	
	7	0.01752	0.03932	0.1242	1.222	0.01575	0.03432	0.1046	0.9983	0.01428	0.03046	0.09079	0.8522
	8	0.01375	0.02778	0.07096	0.3161	0.01251	0.02464	0.06102	0.2629	0.01145	0.02215	0.05370	0.2269

Kutzelnigg [52–54] have proposed that the two-electron atomic states be classified thus: *a two-electron state, composed of one-electron spatial orbitals with individual parities $(-1)^{\ell_1}$ and $(-1)^{\ell_2}$ and hence with overall parities $(-1)^{\ell_1+\ell_2}$, is said to have natural parity if its parity is $(-1)^L$. [...] If the parity of the two-electron state is $-(-1)^L$, the state is said to be of unnatural parity.* [54]

After introducing spin, three classes emerge. In a 3-dimensional space, the states with a cusp value of $1/2$ [55,

56] are known as the *natural parity singlet states*, those with a cusp value of $1/4$ [57] are the *natural and unnatural parity triplet states*, and those with a cusp value of $1/6$ [52], are the *unnatural parity singlet states*.

In previous work [29], we have observed that the $^1S^\circ$ ground state and the first excited $^3P^\circ$ state of 3-spherium possess the same singlet ($1/2$) and triplet ($1/4$) cusp conditions as those for electrons moving in three-dimensional physical space and we have therefore argued that 3-

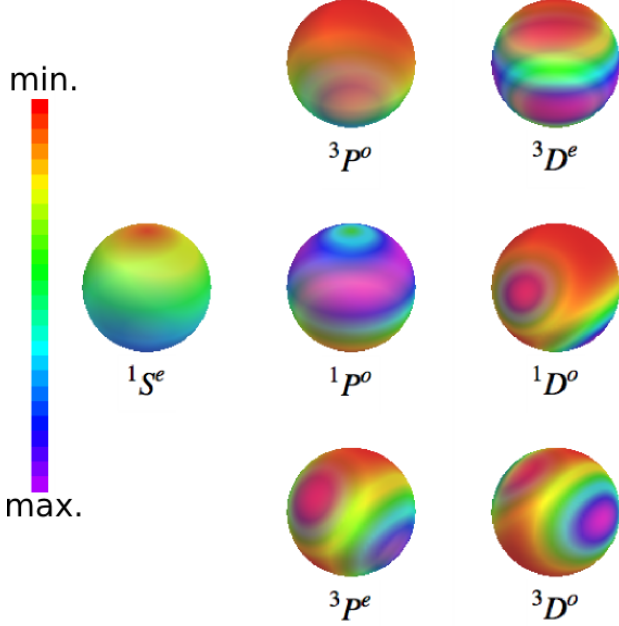


FIG. 2. Density plots of the S , P and D states of 2-spherium. The squares of the wave functions when one electron is fixed at the north pole are represented. The radii are $\sqrt{3}/2$, $\sqrt{15}/2$, $\sqrt{5}/2$, $\sqrt{21}/2$, $\sqrt{21}/2$, $3\sqrt{5}/2$ and $3\sqrt{3}/2$ for the $1S^e$, $3P^o$, $1P^o$, $3P^e$, $3D^e$, $1D^o$ and $3D^o$ states, respectively.

spherium may be the most appropriate model for studying “real” atomic or molecular systems. This is supported by the similarity of the correlation energy E_c of 3-spherium to that in other two-electron systems. Indeed, it can be shown [36] that, as $R \rightarrow 0$, E_c approaches -0.0476 , which is close to the corresponding values for the helium-like ions (-0.0467) [58], the Hooke’s law atom (-0.0497) [59], and two electrons in a ball (-0.0552) [46].

Most of the higher angular momentum states of 3-spherium, possess the “normal” cusp values of $1/2$ and $1/4$. However, the unnatural $1D^o$ and $1F^e$ states have the cusp value of $1/6$.

B. First-order cusp condition

The wave function, radius and energy of the lowest states are given by

$$\Psi_{1,0}(u) = 1 + \gamma u, \quad R_{1,0}^2 = \frac{\delta}{4\gamma}, \quad E_{1,0} = \gamma, \quad (12)$$

which are closely related to the Kato cusp condition [56]

$$\frac{\Psi'(0)}{\Psi(0)} = \gamma. \quad (13)$$

We now generalize the Morgan–Kutzelnigg classification [53] to a \mathcal{D} -dimensional space. Writing the interpar-

ticle wave function as

$$\Psi(u) = 1 + \frac{u}{2\kappa + \mathcal{D} - 1} + O(u^2), \quad (14)$$

we have

$$\begin{aligned} \kappa &= 0 \text{ for natural parity singlet states,} \\ \kappa &= 1 \text{ for triplet states,} \\ \kappa &= 2 \text{ for unnatural parity singlet states.} \end{aligned} \quad (15)$$

The labels of the \mathcal{D} -spherium states are given in Table I.

C. Second-order cusp condition

The second solution is associated with

$$\Psi_{2,0}(u) = \Psi_{1,0}(u) + \frac{\gamma^2(\delta + 2)}{2\gamma(\delta + 2) + 4\delta + 6} u^2, \quad (16)$$

$$R_{2,0}^2 = \frac{(\gamma + 2)(\delta + 2) - 1}{2\gamma}, \quad (17)$$

$$E_{2,0} = \frac{\gamma(\delta + 1)}{(\gamma + 2)(\delta + 2) - 1}. \quad (18)$$

For \mathcal{D} -spherium, the second-order cusp condition is

$$\frac{\Psi''(0)}{\Psi(0)} = \frac{1}{2\mathcal{D}} \left(\frac{1}{\mathcal{D} - 1} - E \right). \quad (19)$$

Following (19), the classification (15) can be extended to the second-order coalescence condition, where the wave function (correct up to second-order in u) is

$$\begin{aligned} \Psi(u) &= 1 + \frac{u}{2\kappa + \mathcal{D} - 1} \\ &+ \frac{u^2}{2(2\kappa + \mathcal{D})} \left(\frac{1}{2\kappa + \mathcal{D} - 1} - E \right) + O(u^3). \end{aligned} \quad (20)$$

Thus, we have, for $\mathcal{D} = 3$,

$$\frac{\Psi''(0)}{\Psi(0)} = \begin{cases} \frac{1}{6} \left(\frac{1}{2} - E \right), & \text{for } \kappa = 0, \\ \frac{1}{10} \left(\frac{1}{4} - E \right), & \text{for } \kappa = 1, \\ \frac{1}{14} \left(\frac{1}{6} - E \right), & \text{for } \kappa = 2. \end{cases} \quad (21)$$

For the natural parity singlet states ($\kappa = 0$), the second-order cusp condition of 3-spherium is precisely the second-order coalescence condition derived by Tew [60], reiterating that 3-spherium is an appropriate model for normal physical systems.

D. Third-order cusp condition

The third-order cusp condition of 3-spherium is

$$\frac{\Psi'''(0)}{\Psi(0)} = \frac{1}{18} \left(\frac{1}{8} - E + \frac{15}{16R^2} \right), \quad (22)$$

which is similar, but not strictly equivalent, to the one derived by Tew [60], due to the R -dependence of (22). The generalization to \mathcal{D} dimensions is straightforward.

E. Interdimensional degeneracies

As shown in Table I, many states of \mathcal{D} -spherium have the same Hamiltonian (7) as lower angular momentum states of $(\mathcal{D} + 2)$ -spherium.

Using the transformation $(\mathcal{D}, L) \rightarrow (\mathcal{D} + 2, L - 1)$ (see Table I), one can see that the Hamiltonian of the $^3P^e$, $^1D^o$, $^3D^o$ and $^1F^e$ states for a given value of \mathcal{D} are respectively identical to those for $^1S^e$, $^3P^o$, $^1P^o$, and $^3D^e$ states at $\mathcal{D} + 2$. The transformation $(\mathcal{D}, L) \rightarrow (\mathcal{D} + 2, L - 1)$, preserves the parity of the states, but “flips” the spin configuration, thereby increasing by one unit the value of κ . In \mathcal{D} -spherium, we note that the Hamiltonians of the $^3P^e$ and $^3D^e$ states are identical.

Similar interdimensional degeneracies, first noticed by van Vleck [61], have been observed for various systems [44, 62–65].

V. CONCLUSION

In this article, we have reported exact solutions of a Coulomb correlation problem, consisting of two electrons on a \mathcal{D} -dimensional sphere. The Coulomb problem can be solved exactly for an infinite set of values of the radius R for both the ground and excited states, on both the singlet and triplet manifolds. The corresponding exact solutions are polynomials in the interelectronic distance u .

The cusp conditions (up to third-order in the inter-electronic distance), which are related to the behavior of the wave function at the electron-electron coalescence point, have been analyzed and classified according to the natural or unnatural parity of the state considered.

Finally, we have shown seen that, as in other one-, two- or three-electron systems, there exist interdimensional degeneracies between some of the states of \mathcal{D} -spherium.

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